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Highlights

- High ammonia concentrations inhibit acetoclastic methanogenesis in FW AD
- Syntrophic acetate oxidation is the main acetate-consuming pathway
- Including syntrophic acetate oxidation improved the performance of the model
- Davies equation for free ammonia estimation led to precise inhibition limits

Abstract: The aim of this study was to assess the importance of two major modifications of the IWA ADM1 on its ability to model food waste anaerobic digestion: (i) estimating free ammonia nitrogen using a modified Davies equation and (ii) including syntrophic acetate oxidation as main acetate-consuming pathway. The obtained results show that, in agreement with the literature, including the Davies equation for free ammonia estimation avoided overestimations of up to 30% when compared to the ideal equation (standard in the ADM1). Further including syntrophic acetate oxidation allowed to properly represent the dynamics of methane production and the volatile fatty acid profiles (*e.g.* propionate accumulation). This also allowed to predict more accurately the structure of the microbial communities (*e.g.* with hydrogenotrophs as dominant methanogens). Combined, these modifications allowed to obtain more precise values of the inhibition constants for different microbial clades. In addition, a threshold inhibition function was used, which allowed a more accurate inhibition representation. Finally, the kLa values were drastically reduced to account for the decreased mass transfer rates. The presented work shows that these modifications must be considered to achieve an accurate representation of food waste anaerobic digestion using mechanistic models. Although further calibration and validations must be performed, the results are promising when considering the high ammonia nitrogen and transient volatile fatty acid concentrations in the reactors and the performance of the unmodified ADM1.

Keywords: Solid waste; High-solids AD; Dry AD; Hydrogenotrophic methanogenesis

Introduction

The production of food waste (FW) is currently a global issue and a huge effort is being put to develop new sustainable technologies for its treatment. Anaerobic digestion (AD) stands as an environmental-friendly alternative that offers a triple role: (i) waste stabilization, (ii) production of renewable energy in the form of biogas and (iii) nutrient recovery by digestate application.

However, AD of highly concentrated substrates such as FW (20% total solids; TS) is a complex biological process prone to failure if not properly managed. Because of the fast biodegradability of FW, accumulation of volatile fatty acids (VFAs) has been frequently reported due to unbalance of the acidogenesis/acetogenesis and methanogenesis steps (Capson-Tojo *et al.*, 2016). In addition, the high protein content of this substrate leads to high concentrations of total and free ammonia nitrogen (TAN; FAN) in the reactors, being the latter toxic to microorganisms, mainly to strict acetoclastic methanogens (Banks et al., 2008; Capson-Tojo et al., 2018b, 2017b). Therefore, if AD of concentrated substrates such as FW is to be modelled properly, the dominant metabolic pathways occurring (*e.g.* syntrophic acetate oxidation (SAO) and hydrogenotrophic methanogenesis (HM)) must be represented accurately (Capson-Tojo *et al.*, 2018a; Rivera-Salvador *et al.*, 2014). Furthermore, special attention must be paid to the TAN-FAN acid-base equilibria, which is affected, not only by the pH and the temperature, but also by the high ionic strength of the media (Capson-Tojo *et al.*, 2020).

The goal of this study was to assess the importance of two major modifications of the IWA ADM1 on its ability to represent FW AD: (i) estimating FAN using a modified Davies equation and (ii) including SAO as predominant acetate-consuming pathway.

Material and Methods

Inoculum and substrate

The inoculum used to start the reactors was collected from an industrial plant treating different organic streams at high TAN/FAN concentrations (5.04 g $TAN \cdot l^{-1}$; 615 mg $FAN \cdot l^{-1}$). The inoculum had an initial TS content of 5.8%, with 59% corresponding to volatile solids (VS). The FW was collected from different producers from the region of the Grand Narbonne, in the south of France. It had a TS content of 21% (90% VS), it was mainly composed of carbohydrates (618 $g \cdot kg\ TS^{-1}$) and it showed relatively low C/N ratios (16.1). A more extensive FW characterization can be found in Capson-Tojo *et al.* (2017a).

Batch anaerobic reactors

Different batch experiments were carried out to calibrate and validate the model. The reactors (in triplicate) were started using 60 g of FW as substrate (raw). The substrate to inoculum (S/X) ratio was set as 1 g $VS \cdot g\ VS^{-1}$ (~30 g VS $FW \cdot l^{-1}$). The vessels were incubated at 37 °C and had an initial working volume of 429 ml. The incubation system was an Automated Methane Potential Testing System (AMPTSII) (Bioprocess Control, Sweden). A more precise description can be found in Capson-Tojo et al. (2018a). The digestate samples were analysed as described in Capson-Tojo *et al.* (2017a).

Model comparison and calibration

Three different models were compared in terms of modelling performance: (i) unmodified ADM1 (Batstone et al., 2002), (ii) ADM1 using the modified Davies equation for FAN estimation presented in Capson-Tojo *et al.* (2020) and the threshold inhibition function from Astals *et al.* (2018), and (iii) model (ii) including SAO, as presented in Rivera-Salvador *et al.* (2014).

To avoid biased comparisons, the modelling procedure was the same for all the approaches. Starting with the same initial working conditions and using the same experimental dataset, manually-calibrated simulations were carried out, using default literature values for the kinetic parameters. In all the simulations, kinetic parameters validated in the literature were kept unmodified when possible. The simulations were carried out using MATLAB R2018b (The MathWorks Inc., Natick, MA).

Results and Discussion

The main results corresponding to the simulations using the ADM1 and the modified model including FAN estimation using Davies, the threshold inhibition function and SAO, are shown in Figure 1. Starting with the inclusion of the modified Davies equation for FAN estimation, its application allowed to correct overestimations of up to 29.6% when compared to the unmodified ADM1, varying according to the pH during the batch experiments. In agreement with Capson-Tojo *et al.* (2020), this result shows that the ideal equation included in the ADM1 overestimates significantly the FAN proportions in highly-concentrated AD systems. Therefore, if accurate inhibition limits (*e.g.* KI_{50} or KI_{min}-KI_{max} values) in concentrated AD reactors are to be obtained via modelling approaches, equations that consider the ionic strength of the media must be used.

Continuing with the importance of including SAO into the ADM1 for proper FW AD modelling, it can be observed in Figure 1 that both models were relatively accurate when reproducing the methane flow rates and the acetate profiles. Nevertheless, to do so, it was necessary to increase the $K_{I,NH3}$ for acetoclastic methanogens used in the unmodified ADM1 up to 0.005 M, a value 3 times higher than the default value and close to values where acetoclastic activity is totally interrupted (Batstone et al., 2002; Capson-Tojo et al., 2020). Therefore, it is clear that the $K_{I,NH3}$ used lacked of any physical meaning and was simply a value needed for simulation purposes. Furthermore, it is possible to observe that the ADM1 failed at representing the profile of VFAs other than acetate when using common

values of kinetic parameters from the literature. Finally, the ADM1 also failed at predicting the predominant microbial clades, as it attributed acetate consumption to acetoclastic methanogens, which were not present in the digestates at the end of the batch experiments (refer to Capson-Tojo et al. (2018a) for more information on the microbial communities).

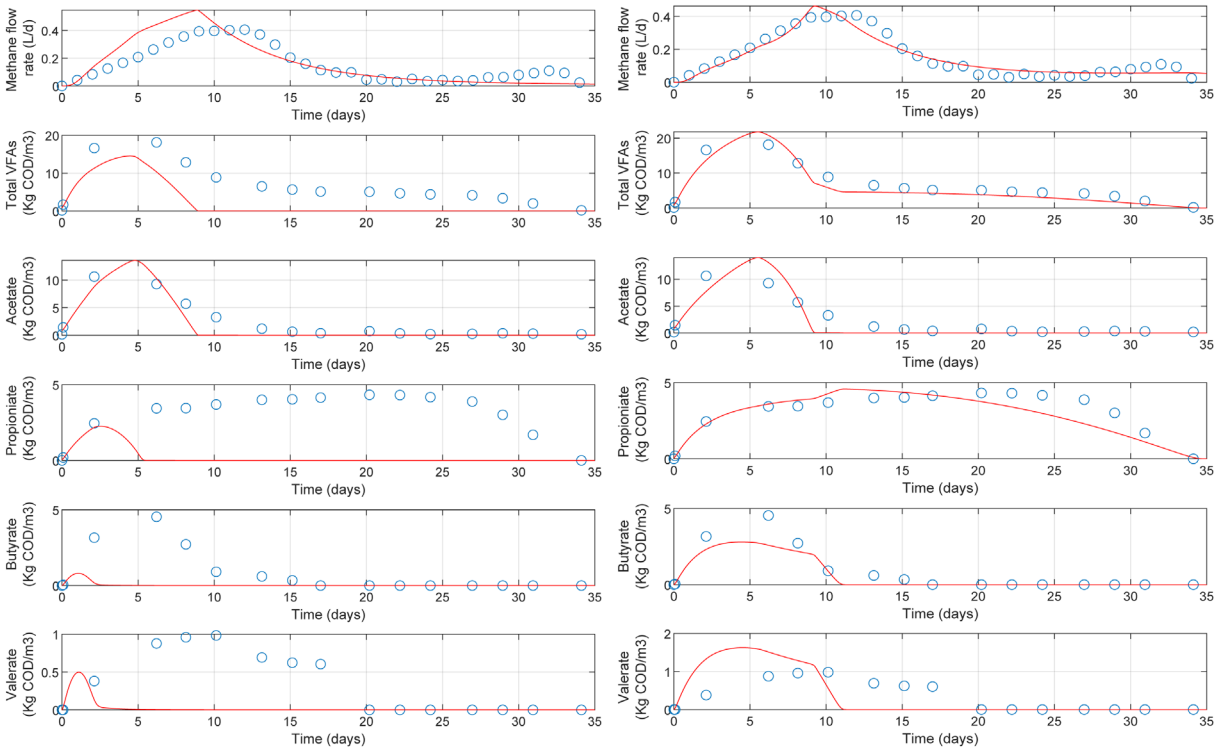

Figure 1 Experimental data and modelling results using (left) the unmodified ADM1 and (right) the modified ADM1 including SAO.

When looking at the performance of the modified ADM1, it is clear that SAO inclusion allowed to represent more accurately the VFA profiles (particularly in the case of propionate), even when using the same kinetic parameters. This enhancement was related to the fact that including SAO affects the hydrogen concentrations in the reactor (as it is a product of acetate consumption), which then influences the consumption of all the VFAs whose consumption is thermodynamically inhibited at high hydrogen concentrations (*i.e.* propionate, butyrate and valerate). The ADM1 does not include SAO, and therefore cannot account for the increased hydrogen contents. Regarding the inhibitory limits used, the values reported in Capson-Tojo *et al.* (2020) for acetoclastic and hydrogenotrophic methanogenesis were directly used (*i.e.* KI_{min}-KI_{max} of 0.006-0.152 g FAN·L^{-1} and 0.175-4.387 g FAN·L^{-1}, respectively), confirming their validity and physical significance, as they were extracted from dedicated inhibition studies. To conclude, the predominant microbial clades predicted by the model (with SAO as acetate consumers, without acetoclastic methanogens and with hydrogenotrophs as main methanogens) agree with the experimental results (see Capson-Tojo et al. (2018a)).

A final comment must be made about the reduction in mass transfer coefficients in high-solids/dry AD systems. This issue has been previously reported to practically eliminate any convective transfer, reducing also the diffusion transfer coefficients (Bollon et al., 2013). In our study, this was reflected on the used volumetric mass transfer coefficients (kLa) values, which were reduced in all models to 0.2 d^{-1} (*vs.* the default value of 200 d^{-1}). Proper gas diffusion modelling is crucial, as this affects the concentrations of species in the liquid phase (hydrogen being particularly relevant) and the pH.

It is important to note that the kinetic constants for VFA uptake were the same in both simulations, and equal to the recommended values for mesophilic AD in the ADM1 (Batstone et al., 2002). Only

the hydrogen uptake rate was reduced in both models (from 35 to 20 d^{-1}). This excludes enhanced performances due to more precise calibrations.

Conclusions

Although further dynamic calibrations and validations are needed, the obtained results suggest that including SAO as acetate-consuming process is crucial for a proper mechanistic modelling of FW AD. This allowed to properly represent the VFA profiles during the experiments, which was not possible using the unmodified ADM1 structure (particularly in the case of propionate). In addition, the precise estimation of the FAN levels in the system via the application of the modified Davies equation allowed to avoid significant overestimations of the FAN concentrations (up to 30%). This allows to precisely calculate inhibition coefficients. Finally, the kLa values were drastically reduced to account for the decreased mass transfer rates. Overall, the modifications done improved considerably the predictions/simulations of the performance and the predominant microbial clades (particularly relevant for methanogenesis and acetate consumption). This is of clear relevance for both academic and industrial actors working on FW AD.

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